# THE USE OF FIBRE OPTIC PROBES FOR FLOW MONITORING WITHIN A SMALL-SCALE TUBE

N. Reis*, A.A. Vicente*, J.A. Teixeira*, M.R. Mackley[o]

*Centro de Engenharia Biológica, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal, Phone: +351.253.604400, Fax: +351.253.678986, E-mail: avicente@deb.uminho.pt
[o]Department of Chemical Engineering, University of Cambridge, New Museum Site, Pembroke Street, CB2 3RA Cambridge, UK, Phone: +44(0)1223.334777, Fax: +44(0)1223.334796, E-mail: mrm1@cheng.cam.ac.uk

## ABSTRACT

This paper demonstrates the effectiveness of using fibre optic micro-probes for the measurement of dispersion and mixing in continuous flow within small-scale tubes under oscillatory flow conditions.

The experimental data was modelled and compared either by three different well-known non-ideal models: a) tanks-in-series (with no backflow); b) differential backmixing; c) stagewise backmixing, and by one two-parameter flow model consisting of a plug flow and a stirred tank reactor in series. Model parameters were found by fitting the theoretical response with experimental data in both Laplace and time domains by different methods.

In addition, specific results are presented relating to a small scale tube provided with smooth periodic constrictions (SPCs), the basic element of a novel screening reactor presented by Harvey et al. (Proceedings of the ECCE-4, Granada (2003) 0-6.4-004). The unsteady tracer injection technique was used at different oscillation conditions, with oscillation frequencies from 0 to 20 Hz and amplitudes from 0 to 3 mm (centre-to-peak). An intermediate mixing behaviour (between plug flow and stirred tank reactor) was achieved in that range of oscillation frequencies and amplitudes. Dispersion was found to be dependent on the oscillation conditions (amplitude and frequencies) and related with the fluid backflow and with the breaking of flow symmetry. The discrete (stagewise) backmixing model was considered as the best model representing residence time behaviour in the small-scale tube.

## INTRODUCTION

A small-scale tube provided with smooth periodic constrictions (SPC) and presenting a reduced volume (about 4.5 ml) compose a novel continuous screening reactor based on oscillatory flow technology [1]. That reactor was recently presented in Harvey *et al.* [2] as a new small-scale geometry for reaction engineering and particle suspension applications. Experimental studies using Particle Image Velocimetry (PIV), validated by Computational Fluid Dynamics (CFD) [2] have shown different fluid flow patterns originated at different oscillation conditions (oscillation frequencies and amplitudes) and a near plug flow or a completely mixed behaviour can be approached just by setting the oscillation conditions. Thus, a deeper knowledge of the flow behaviour within this small-scale tube and its dependence on the oscillation conditions is desired. Due to the low level scale, refined techniques are required for accurate measurements of residence time distributions (RTD).

For continuous processing devices, the tracer injection and response method has been widely used to study mixing characteristics of reactors [3]. Techniques such as the moment [4], weighted moment [5], Laplace and Fourier transform domain analysis [6] and time domain analysis [7, 8] have been employed to analyze the tracer response data. A good discussion of the advantages and disadvantages of each technique may be found in Froment and Bischoff [9]. Time domain analysis of residence time distribution (RTD) in baffled tubes such as conventional oscillatory flow reactors (OFRs) has been reported by several authors [10-14] using conventional techniques (e.g. conductivity measurement). The main problem with such technique is the effect of the tracer density (solution of NaCl or potassium nitrite) which affects the sensitivity of the determination. More recently Fitch and Ni [15] applied a non-intrusive *state-of-the-art* laser induced fluorescence technique (using a dye that fluoresces when induced by a laser) to study the RTD in conventional OFRs and concluded that intrusive experiments using conductivity probes can have problems of mass transfer into the membranes of the probes, leading to misleading results. In most of the studies available, two different models were used to determine dispersion coefficients: a) plug flow with axial dispersion and b) continuous stirred tank reactor (CSTR) with backflow. Similar results were achieved by both methods.

It has been proposed by Briens et al. [16] that high differences can exist between the real RTD curve and a concentration profile measured by a "through the wall" technique (instead of "mixed cup" concentrations) when flow behaviour is far from plug flow. This usually leads to errors in the determination of liquid residence times by the tracer injection technique. Thus, a correct specification of the system boundaries is of vital importance.

In the present study the RTD behaviour in a small-scale tube was proposed to be determined using the conventional unsteady tracer injection technique but eliminating some of its pitfalls [17] by applying a more refined optical method of tracer detection such as optical fibre micro-probes. In the interpretation of RTD curves, the flow behaviour was tested by several models that usually represent intermediate mixing behaviours: a) series of CSTRs without interactions [18], b) two-parameter model consisting of a series of one plug-flow and one completely mixed region [18], c) differential model and d) stagewise models [19]. The last two comprise fluid backflow. Dispersion was expressed by model parameters, fitted to experimental tracer concentration along the time at Laplace and time domains by different methodologies and according to the system boundaries (open or closed system).

## METHODS AND MATERIALS

### The Small-Scale Tube

The small-scale tube is a 4.4 mm internal diameter and 350 mm long jacketed glass tube with an operational volume of c.a. 4.5 ml and provided with smooth periodic constrictions (SPCs). The average distance between adjacent constrictions is

13 mm and the decrease on the free area of such constricted zones is of 87 %. Mean (cross-section weighted) tube internal diameter is about 4.0 mm. A single SPC tube is shown in Fig. 1.

## Experimental Apparatus

One SPC tube was fixed vertically and mounted according to Fig. 2. Flow rate was achieved by coupling a net flow from a peristaltic pump (Fig. 2, 1). The inlet stream from the peristaltic pump was passed through a reservoir in order to eliminate propagation of fluid pulsations (Fig. 2, 2). Oscillations were achieved by a rotative ceramic piston pump (CKCRH0, Fluid Metering Inc., New York), working in closed-loop. The design of such pump (valveless rotating and reciprocating piston) allowed good sinusoidal oscillations of the fluid. The control of oscillation amplitude of the fluid was made by turning an easy-grip flow control ring in the pump head. The relation between piston position ($h_p$) and fluid amplitude ($x_0$) was: $x_0$ (mm centre-to-peak) = 7.3074E-3 $\times$ $h_p$. Oscillation amplitudes from 0 to 3 mm were obtained. All values of amplitude express the centre-to-peak oscillation of the fluid in the maximum internal tube diameter zone (4.4 mm). The oscillation frequency was controlled by the angular rotation of a motor (as shown in Fig. 2, 3). The range of interest for the oscillation frequencies was from 0 to 20 Hz. In all, a precise control of both oscillation amplitude and frequency was obtained.

The coloured tracer used in the experiments was an aqueous solution of Indigo carmine obtained from Merck (Darmstadt, Germany). This substance was selected as it did not adsorb to both the installation pipes and the SPC tube walls. It has a maximum optic absorption between 610 and 612 nm.

Experiments were prepared by continuously injecting an aqueous solution of 0.2 kg/m$^3$ of tracer in a SPC tube through a tracer injection port (Fig. 2, 14). Once the concentration was stable, the tracer injection was stopped. Fresh water was subsequently pumped through the inlet of the SPC tube by turning on the peristaltic pump (the starting point of the experiments, i.e. $t$ = 0) until the concentration of tracer becomes null at the exit, leading to a negative step injection at the inlet. Tracer concentrations were monitored at real time by means of a fibre optic system (see next section for further details). Readings were made each 1/9$^{th}$ of a second and each three consecutive readings were averaged resulting in experimental points available at each 1/3$^{rd}$ of a second. All experiments were performed at room temperature (20 ºC) and using distilled water as main fluid.

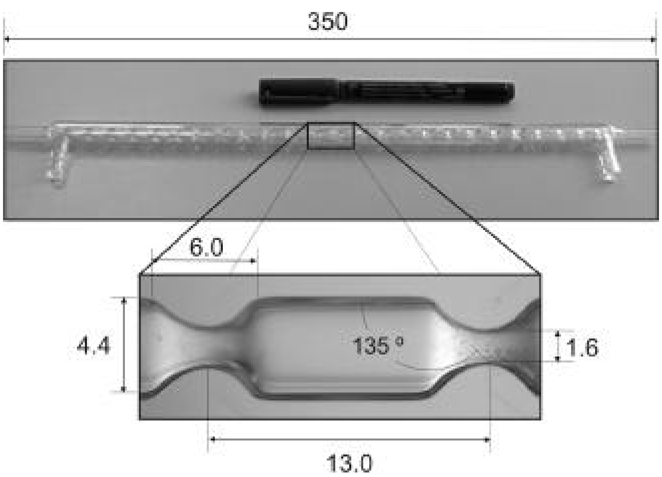


Fig. 1: Geometry of a single SPC tube (all units in mm).

## The Fibre Optic System

On-line tracer concentration was measured by means of optical micro-probes connected to a multi-channel optic spectrometer system (Avantes, Eerbeek, The Netherlands). Due to the geometry of the SPC tube (small scale and closed system), two different probes were used. A micro transmission dip optical probe (FDP-UV-micro-1), with 2 mm optical length, was used to monitor the (local) tracer concentration inside the first cavity of the SPC tube (Fig. 2, 6) at an axial distance of 15 mm from the inlet. At the outlet (axial distance of 358 mm from the inlet point), a reflection probe (FCR-7UV200-1,5x100-2) with a small tip (1.5 mm) was installed perpendicularly to the flow direction (Fig. 2, 7), into a 5 mm internal diameter in-line flow cell with white walls (Fig. 2, 9). The reactor was covered with aluminium paper at the measuring points in order to reduce the noise due to environmental light (Fig. 2, 8). Both optical probes were provided with SMA connectors.

Reading of the light coming from both probes was made on-line and simultaneously using slave1 and slave2 channels of a 4-channel optical spectrometer AvaLights-2048 (Fig. 2, 12). The CCD detector was connected to an electronic board with 14 bit AD converter and USB/RS-232 interface. Data transfer between the optic spectrometer and a personal computer (Fig. 2, 13) was controlled by AvaSoft full software.

The response of the system was found to be highly linear at tracer concentrations up to 0.3 kg/m$^3$ for the transmission probe and up to 1 kg/m$^3$ for the reflection probe.

## Intermediate mixing flow models

Most transfer and reaction processes are more efficiently executed under plug flow than mixed conditions. However, non-ideal flow is commonly obtained in industrial equipments. Such deviations can be e.g. due to channelling, dead zones or

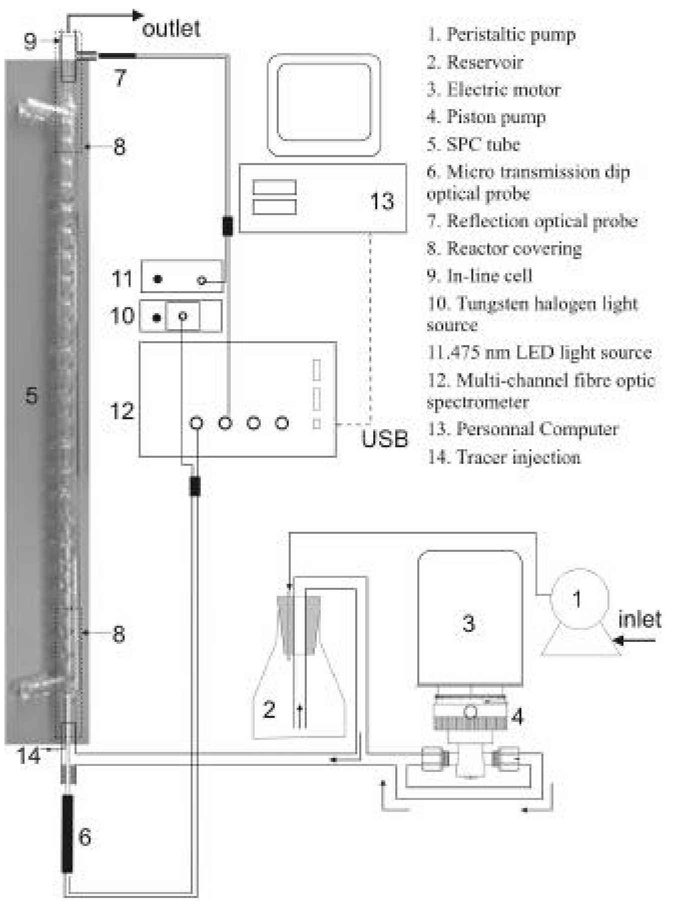


Fig. 2: Experimental apparatus for RTD studies.

backflow. In the case of the SPC tube, the dispersion is mainly due to the nature of the oscillatory flow mixing along the tube. Several theoretical models have been developed in the past to characterize intermediate mixing states. In the present study, three models for non-ideal flow and a two-parameter model were considered for RTD characterization of flow in a SPC tube: a) tanks-in-series model [18]; b) differential backmixing model [19]; c) stagewise backmixing model [19] ($N_{sw}$ = 26) and d) a two-parameter model, the parameters being $V_p$ and $V_m$. A schematic representation of the SPC tube according to each hydrodynamic model is presented in Fig. 3. Characteristic equations (transfer function, mean time and variance) of each considered model may be found in Levenspiel [18] and Mecklenbergh and Hartland [19].

In terms of boundaries of the system, since the injection and the outlet concentration measurement were performed in sections without constrictions (plain tube) a plug flow was assumed in both inlet and outlet sections. Such are the so-called "closed-closed" boundary conditions, meaning that a fluid element can enter and leave the SPC section only once. This simplification was considered because no significant mixing is assumed to occur on the plain sections of the tube when compared with the mixing rates inside the cavities. This also means that the linear average concentration measured at the outlet point by the reflection optical micro-probe (which usually leads to through-the-wall concentrations) may be interpreted as a mixing-cup concentration and that the direct response at the outlet is the *F*-diagram (cumulative concentration).

**Pulse Response Moments**

The first step for dispersion parameter estimation was the determination of the moments that characterise the response of each probe. The most important moments of the C-curves are the first and the second ones, leading to the determination of

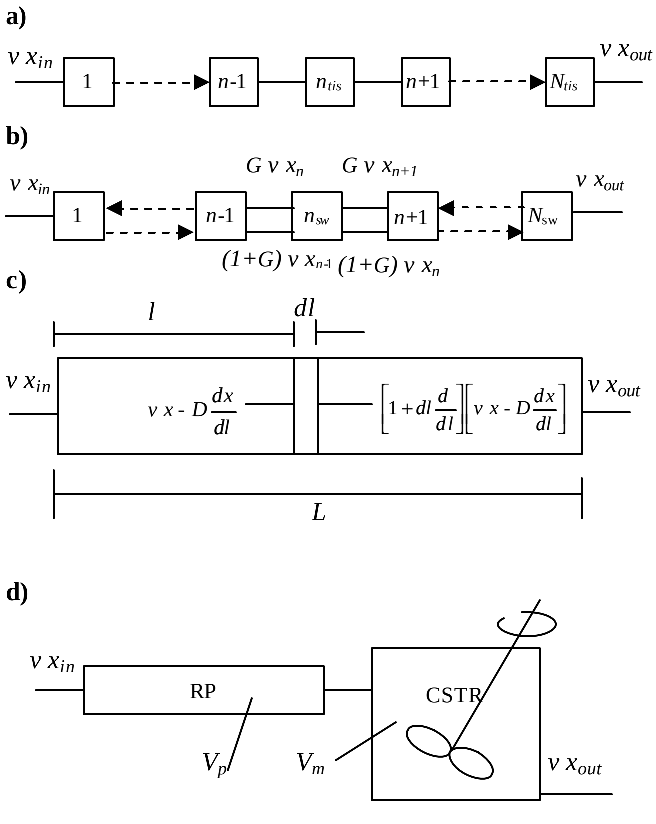


Fig. 3: Schematic representation of flow in: (a) tanks-in-series; (b) a differential reactor with backmixing [19]; (c) *N* stages with backmixing (the mass balance is presented for stage *n*) [19]; (d) two-parameters model composed of a single plug-flow and a single mixed region connected in series.

the mean residence time, $\bar{t}$, and the variance, $s^2$, of the tracer, respectively. The general equation for determination of a *k*th moment $MO_k$ is:

$$MO_k \equiv \int_0^\infty t^k E(t)\,dt \qquad (1)$$

where $E(t)\,dt$ represents the fraction of fluid elements that enters the reactor at $t = 0$ and leaves the reactor between $t$ and $t + dt$ [20]. In terms of statistics, as presented by Danckwerts [21], it represents the probability for a fluid element to have a residence time in the reactor between $t$ and $t + dt$.

For a positive step input, it can be easily demonstrated that Eq.(1) becomes:

$$MO_k = \int_0^{x_{in}} t^k \frac{1}{x_{in}}\,dx \qquad (2)$$

Thus, the mean residence time, $\bar{t}$, can be directly obtained from Eq.(2) by setting $k = 1$. Also the spread in residence time (characterised by the variance, $s^2$) can be obtained from the first and second moments ($MO_1$ and $MO_2$, respectively) according to Eq.(3) [20].

$$s^2 = MO_2 - MO_1^2 \qquad (3)$$

**Estimation of Model Parameters**

Four different methods were applied in the determination of dispersion parameters from residence time distribution functions. The selected methods covered a wide range of levels of computation requirements and simplifications. An iterative process was done both in Laplace and time domains (for models where time-solved equations were available) and considering either a perfect or an imperfect impulse at the inlet. Also the sensibility of the parameter estimation in relation to the considered system boundaries was tested. The fitting techniques (a, b, c and d) were:

(a) Comparison of the numerical Laplace transform, $\mathcal{L}(x)$ or $g(T)$, of the model with that of the pulse response, $g_{out}(T)$ around a point of $T$ ($T_{ref}$) that suppresses the effect of the exponential term (tail). In Laplace's domain, the response at a specific point of a system can be represented by the product of the inlet times a *transfer function*, $g(T)$, which is unique for each system and can be obtained from a mass balance. It has been widely demonstrated [19] that:

$$\bar{x} = \bar{x}_{in}\; g(T) \qquad (4)$$

where $\bar{x}$ is the integral convolution of the measured concentration $x$ in a specific point of the system (e.g. at the exit) and is given by Eq.(5).

$$\bar{x} = \mathcal{L}(x) = \int_0^\infty e^{-Tq}\; x\,dq \qquad (5)$$

where $q$ is the dimensionless time ($t/\bar{t}$).
The experimental transfer function at the exit, $g_{out}(T)$, was obtained applying Eq.(4) to the experimental data acquired by the refection probe located at the exit of the SPC tube. In terms of inlet, the calculation of $\bar{x}_{in}$ in Laplace domain for a negative step input is a non trivial task. Thus, experimental data of concentration $x$ was firstly converted to $[x_0 - x]$. All the following calculations become thus simplified and a positive step

can now be considered. The Laplace transform of the perfect (positive) step input is presented in Eq.(6).

$$\bar{x}_{in} = \frac{(x_{out})_\infty}{T} = \frac{x_0}{T} \tag{6}$$

Since only discrete points were available, the estimation of model parameters by this technique required the discretisation of Eqs. (5) by the Simpson rule. This also involved that the following function had to be minimized in order to determine the best fitting of experimental data to theoretical models around the selected value of $T$ ($T_{ref}$):

$$\Delta = \int_{0.5T_{ref}}^{2T_{ref}} \{g(T) - g_{out}(T)\}^2 dT \tag{7}$$

(b) Comparison of the moments of each hydrodynamic model (derived from the transfer function of the model) with those of the pulse response. This avoids the curve fitting procedure. It can be demonstrated that the calculation of mean time and standard deviation is reduced to the form presented in Eq.(8) and Eq.(9) below, respectively [19], if a perfect step input is considered at the inlet.

$$\bar{q} = -\left[\frac{\partial \ln g}{\partial T}\right]_{T=0} \tag{8}$$

$$s^2 = \left[\frac{\partial^2 \ln g}{\partial T^2}\right]_{T=0} \tag{9}$$

(c) Comparison of the numerical Laplace transform $g(T)$ with the pulse response found at two different points (e.g. the outlet and one internal position). This method usually permits to eliminate the effect of the tail and to consider an *imperfect step input*. From experimental results (discrete points), $\bar{x}$ and $\bar{x}_{out}$ were determined and related to theoretical transfer function as presented in Eq.(10).

$$\frac{\bar{x}}{\bar{x}_{out}} = \frac{g(T)_{point=z}}{g(T)_{out}} \tag{10}$$

The main feature of Eq. (10) is that the overall equation of $g(T)$ to be fitted is simplified as can be found in Mecklenbergh and Hartland [19].

(d) Time domain fitting: since obtaining analytical solutions for time equations of some models (especially for the stagewise backmixing model) is a hard and unmanageable task, only two models were tested in time domain: a) tanks-in-series and b) differential backmixing model. For tanks-in-series model a perfect step input was considered together with closed-closed boundaries. In the case of the differential backmixing model the only situation where the C-curve can be derived analytically is considering an open vessel. This was not the considered situation for the SPC tube, as referred above, but it was very useful in testing the possible effect of the closed boundaries simplification and consequently the measuring procedure. The analytical equation presented by Levenspiel [18] considered three main simplifications: i) open vessel boundaries; ii) a large extent of dispersion and iii) through-the-wall concentrations. Since both models may deviate from the experimental response, a best fit criterion was required: the $F$-diagram (for dimensionless time) of non-ideal flow models was compared with that of the pulse response. The following goal function was then minimized:

$$\Delta = \int_0^\infty \{F(q) - F_{out}(q)\}^2 dq \tag{11}$$

Experimentally, the major drawback of techniques a), b) and d) is that it is almost impossible to obtain a perfect impulse. However, the use of the step technique minimizes the effect of such simplification over the overall calculations when compared with the impulse technique, since the mean time of injection is almost insignificant when compared with the step input.

## RESULTS AND DISCUSSION

In the present study, about one hundred different experiments were performed at different oscillation conditions (oscillation amplitudes and frequencies). All experiments were performed at a constant net flow rate of 1.94 ml/min. Once the concentration *verus* time (C-curve) was obtained, the moments of the curves (the residence mean time, $\bar{t}$, and the variance, $s^2$) were then calculated. Since only discrete points were available, Eq. (2) was discretised according to Simpson rule. Averaged mean residence times of the tracer within a SPC tube at different oscillation conditions are shown in Fig. 4. Time was then turned dimensionless ($q = t/\bar{t}$) and the quantity of the tracer represented in cumulative $F$-diagrams. Two typical $F$-diagrams are presented in Fig. 5 (a) and Fig. 5 (b). Fluctuations of transmittance probe signal (Fig. 5 b) probably were due to micro-mixing fluctuations or bubbles interference.

### Comparison of different fitting techniques

As previously mentioned, parameters were fitted by different methods and according to different hydrodynamic models, either in time and Laplace domains.

<u>Time domain analysis:</u> $F$-diagrams in Fig. 5 (a) and (b) show the evolution of cumulative (dimensionless) concentration of tracer both in the first cavity (transmission dip probe) and at the exit (reflection probe) of the SPC tube. The presented values correspond to the best fit. In terms of fitting quality, both tanks-in-series and differential backmixing equations in time domain fitted very well $F$-diagrams at low-intensity oscillation conditions, i.e. low oscillation amplitudes

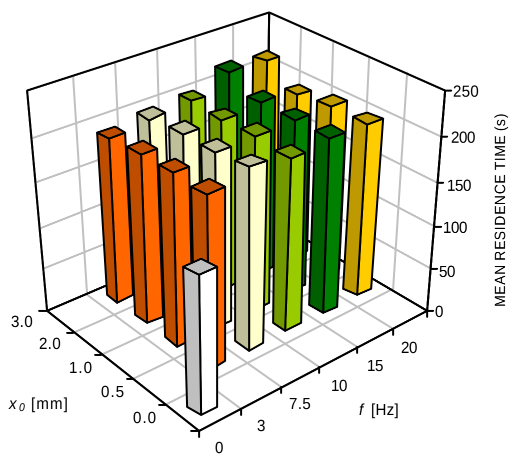


Fig. 4: Vertical bar representation of average mean residence times (s) of the tracer at the outlet of a SPC tube at different oscillation conditions. Net flow rate of 1.94 ml/min.

and high frequencies (Fig. 5 (a)). However, at high-intensity oscillation conditions (essentially high oscillation amplitude) agreement is poor in both cases and the differential backmixing model fails to characterise the flow behaviour within the SPC tube. At those oscillation conditions, the fluid approaches a completely mixed state: the concentrations near the inlet and at the outlet become very similar and the flow within the SPC tube approaches that of a single CSTR (Fig. 5 (b)).

In terms of quantity (magnitude) of the best fitted values, similar values of axial dispersion expressed by the dimensionless Peclet number $P$ were found with tanks-in-series model either in time and Laplace domains (see following section) but higher values of $P$ were obtained with the analytical equation of the differential model in time domain. This is certainly related with the derivation procedure of the analytical equation, mainly with the open vessel boundary condition. The increase on the intensity of oscillation (by increasing the oscillation amplitude or frequency) may eventually lead to some backflow of tracer through the inlet and/or the outlet. However, the degree of that backflow is insignificant when compared with the backflow within the constricted zone of the tube. Consequently, flow at inlet and outlet zones (plain pipe sections) can be considered to behave as a plug-flow and invalidates the through-the-wall concentrations condition. Therefore, the analytical time domain equation presented by Levenspiel [18] tends to overestimate the Peclet number (thus underestimating the axial dispersion) in the SPC tube. Comparison of $P$ values presented in Fig. 5 (a) and (b) with those in Fig. 5 (c) and (d) confirms this (see following section for comments) and is coherent with Briens et al. [16] conclusion.

Laplace domain analysis: finding of best fitting values in Laplace domain by technique a) was limited to a small range of values of $T$ around a reference value, $T_{ref}$. (see section Methods and Materials). Best fitted parameters found for the four different hydrodynamic models at the same oscillation conditions of Fig. 5 (a) and (b) are presented in Fig. 5 (c) and (d), respectively. Slightly different values of parameters were found when compared with time domain fitting (Fig. 5 (a) and (b)). In general, coherent values $P$ (Peclet number) were found with all fitting techniques in Laplace domain (techniques (a) to (c)).

The differential backmixing model successfully fitted RTD of a single SPC tube at all the tested oscillation conditions in Laplace domain. A comparison of best fitted values of $P$ by techniques a) to c) (all in Laplace's domain) for the differential model is presented in Fig. 6. Values of $P$ of similar order of magnitude were obtained using direct Laplace transfer functions considering either a perfect (method a) - Fig. 6 a)) or an imperfect (method c) - Fig. 6 c)) pulse technique. However, the imperfect pulse technique seems to under-estimate high values of $P$. Differences in the order of 30 % were obtained. However, it must be noted that the concentration measured within the first cavity of the SPC tube (near the inlet) may be just a local concentration, especially when it can not be considered homogeneous within the cavity due to poor mixing conditions; at high mixing rates, that "local" concentration effectively represents the mean concentration within the first cavity (or stage) and thus fitting method c) gives results in good agreement with other fitting techniques, thus validating the perfect step assumption at the inlet.

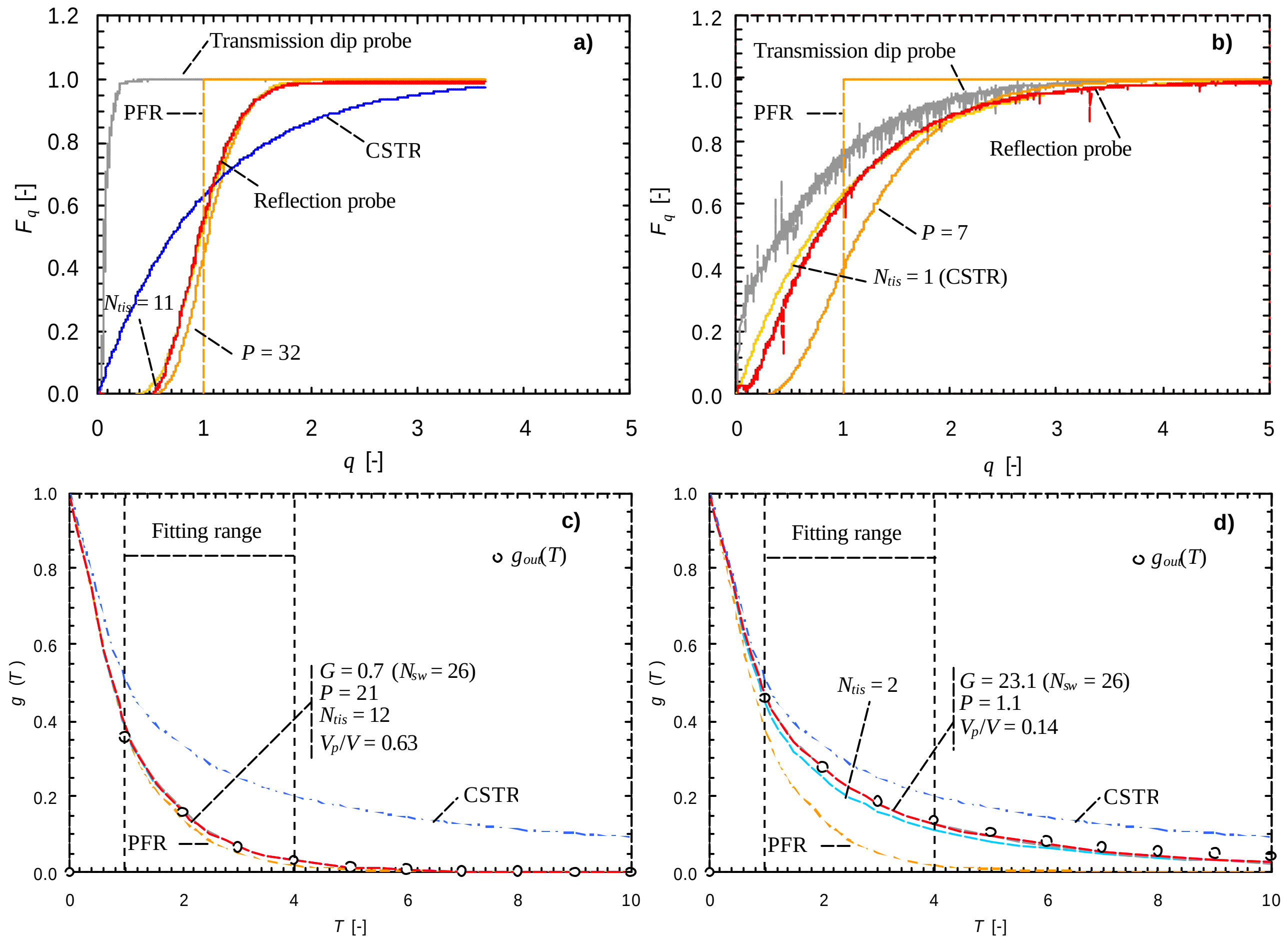


Fig. 5: Best fitted parameters in (dimensionless) time (fitting technique d)) – graphs a) and b) – and Laplace (fitting technique a)) – graphs c) and d) – domains when fluid is oscillated at: (a) and (c) 3 Hz and 0.3 mm; (b) and (d) 20 Hz and 3 mm. Only fitting of reflection probe response signal (at the exit of the SPC tube) is presented since a perfect step change of concentration was considered at the inlet. In (a) and (b) typical $F$-diagrams of the response of the transmission (inside the first cavity) and reflection probes are shown. Net flow rate of 1.94 ml/min. Fitting criterion: Eqs. (6) and (11).

Best fitted $P$ values using the moments technique (Fig. 6 (b)) derived from the transfer function (see Mecklenbergh and Hartland [19]) were quite similar to those values estimated by the transfer function (technique a)). Small deviations were found only at low axial dispersion conditions (high values of $P$). At those conditions, $P$ values were over-estimated up to 7 %, which may be due to the effect of the tail of the C-curves. The moments fitting technique tends to emphasize the data for large values of time and these data are those in the tail of the C-curves, which are usually not very accurate. The main advantages of that fitting method were the easy computation and the direct derivation from the Laplace transform equations while the principal pitfall was the lack of knowledge of the quality of the fit of the model.

In general, fitting method a) gave the most coherent results and thus it was considered the best technique for estimation of axial dipersion. The main disadvantage of this fitting technique (using transfer functions, $g(T)$) was the need to select a $T_{ref}$ value, which is usually around 1. In the present work, the value of $T_{ref}$ was 2.0 and was selected after a study of its effect over the values of the parameters to be estimated (results not shown here).

**Comparison of different hydrodynamic models**

Differential and stagewise backmixing models are inter-convertible and so a relation theoretically exists between the Peclet number, $P$, and the backmixing ratio, $G$: $G + 0.5 = n_{sw} / P$ [19]. That relation was applied to experimental $P$ and $G$ parameters obtained from the backmixing models (results not presented) and the best fitting was achieved by direct fitting of $g(T)$ to $g_{out}(T)$, i.e. by method a). In that case, the obtained cross correlation coefficient, $R$, was equal to 0.9993. However, the imperfect pulse technique (method c)) and the moment technique (method b)) failed that relation by 4 and 11 %, respectively. This stresses the good accuracy of fitting method a).

The stagewise backmixing model was the non-ideal flow model envisaged to represent RTD in a SPC tube due to its natural analogy with the geometry of the tube (number of stages equal to the number of cavities, i.e. 26) and the nature of the oscillatory flow.

In general, the tanks-in-series model (with no backflow) fitted very well the experimental data at the lowest amplitudes but it completely fails to express the RTD behaviour of a SPC tube at the highest oscillation amplitudes. Despite of the very good agreement of values found by the fitting techniques a), b) and d) (Fig. 7), this model has shown (e.g. see Fig. 5) not to be suitable to characterise RTD behaviour over the entire studied range of oscillation conditions within a SPC tube. This is undoubtedly related with the observed high backflow rates (improved at high oscillation amplitudes) which are not

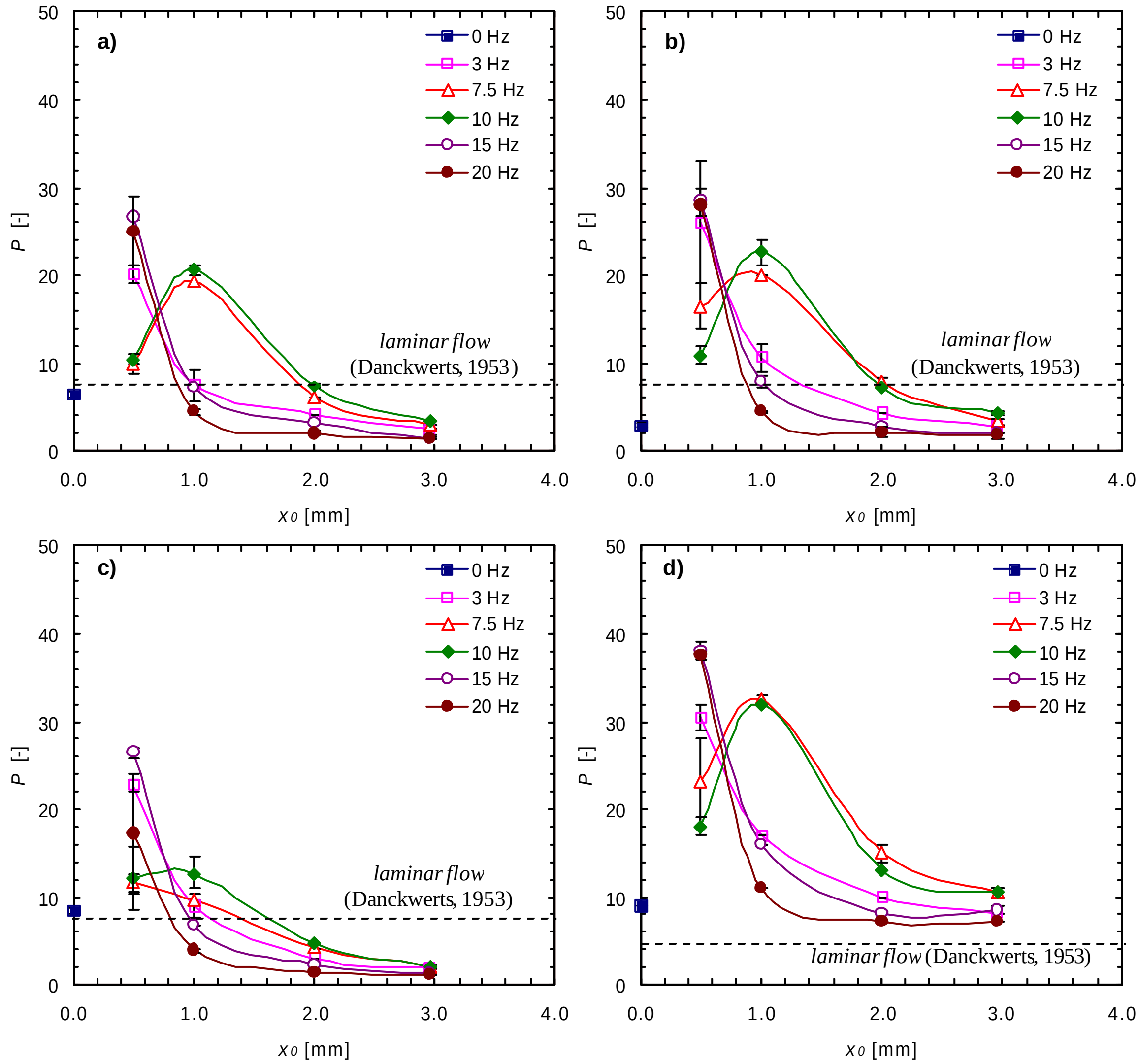


Fig. 6: Best fitted dimensionless Peclet number $P$ obtained according to the differential backmixing model by four different fitting techniques: *a)* Laplace transforms, considering a perfect step input; *b)* pulse response moments (from Laplace transfer functions); *c)* considering an imperfect step input, at Laplace's domain; *d)* time domain, considering a perfect step input and "open-open" vessel boundaries. Fitting techniques a) to c) considered a closed vessel. Net flow rate of 1.94 ml/min. Best possible theoretical approach to plug flow: $P$ = 49.

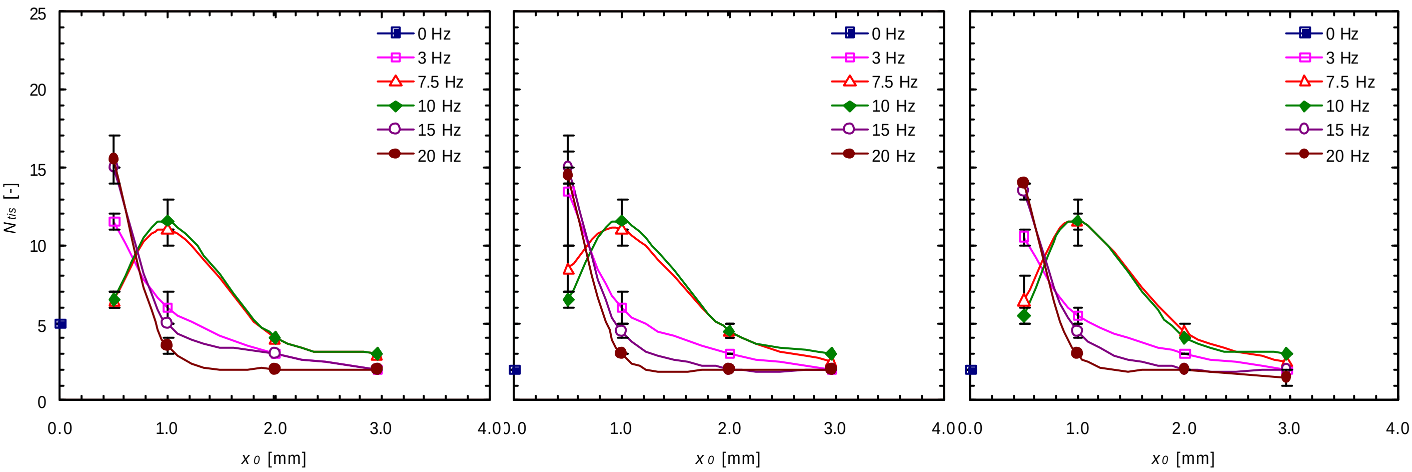


Fig. 7: Best fitted number of tanks-in-series $N_{tis}$ (with no backflow) to experimental data by: *a)* Laplace transforms, considering a perfect step input; *b)* pulse response moments; *c)* time domain, considering a perfect step input and "open-open" vessel boundaries. Graphs a) and b) considered closed vessel. Net flow of 1.94 ml/min. Best theoretical approach to plug flow: $N_{tis}$ = 26.

considered in the tanks-in-series model (Fig. 3 a)).

The two-parameter model (only tested in Laplace domain) presented a very good fit to the experimental data for all the tested oscillation conditions (Fig. 8). This model presented no extended tail in the *C-curve* which renders it less sensitive to the selection of an adequate $T_{ref}$ value. The single parameter used ($V_p/V$) coupled with a good fitting suggest possible application to represent the RTD behaviour of a SPC tube. A small disadvantage when compared with the stagewise model is the absence of a physical meaning for the parameter $V_p/V$ as it works as a "black-box" model. Its main weakness is that it can only be used to predict RTD behaviour at one single point: the reactor outlet.

## Interpretation of fluid mixing within a SPC tube

In Fig. 4 the averaged mean residence time $\bar{t}$ of the tracer (in the operating volume) is presented. The effect of oscillation conditions (oscillation frequency and amplitude) is not significant and the average mean residence time is about 200 s as seen in Fig. 4. However, it should be remembered that the used flow rate corresponds to an average hydraulic time $t$ of ca. 135 seconds ($t = V/v$), which is about 32.5 % lower than the average mean residence time of the tracer. This means that the tracer was effectively lagged within the cavities of the SPC tube and can possibly be explained by the existence of volumes of fluid retained within vortices for finite times. This is in accordance with PIV and CFD results reported by Harvey et al. [2]: very intensive vortices rings are formed under oscillatory flow conditions. In the absence of oscillations (at steady flow), a big eddy exists near the walls of each SPC and the tracer flows through the stream line of the middle of the tube. Thus, since radial mixing is negligible, the tracer is effectively lagged by those eddy structures. With the improvement of radial mixing by the introduction of oscillatory flow, stronger eddy structures develop in the fluid thus temporarily trapping the tracer and delaying its exit from the tube.

Usually, values of $P$ above 1 mean a behaviour near that of a CSTR, while values of $P$ above 50 mean a behaviour near that of a PFR [19]. In the case of the SPC tube, the best possible theoretical approach to plug flow (i.e. consisting of 26 tanks-in-series with no backflow) will be achieved at a value of $P$ equal to 49. In fact, the SPC tube presents an intermediate behaviour for all the studied range of oscillation amplitudes and frequencies (Fig. 6) and it was clear the existence of a dependency between backmixing and $Re_o$ (results not shown here).

Starting from a non-oscillating state, the introduction of oscillations at low amplitudes and low frequencies led to a decrease of the backmixing ratio $G$ (results not shown here) and a consequent increase of $P$. This is related with the increase of intensity of the vortex rings generated inside the

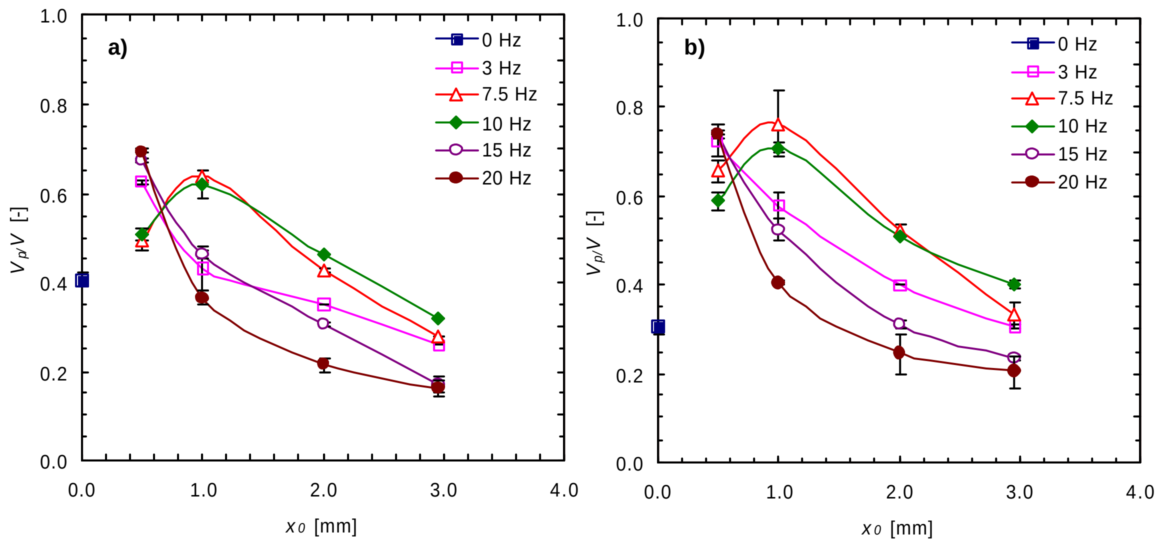


Fig. 8: Best fitted values of $V_p/V$ of the two-parameter model considering a perfect step input by: *a)* Laplace transforms; *b)* pulse response moments. Net flow of 1.94 ml/min. Fitting criterion: Eq. (6). Ideal plug flow: $V_p/V$ = 1.

cavities of the reactor, leading to high radial mixing rates, decreasing the overall backmixing. It was observed that an increase of the oscillation frequency does not affect the dispersion as significantly as an increase of the oscillation amplitude does. In general, the effect of oscillation frequency over the axial dispersion was found to be negligible and the oscillation amplitude appears to be the main factor. Mackley and Ni [10] reported similar conclusions in the study of a conventional OFR. In the case of the SPC tube, the main exception was for the experiments performed at $Re_o$'s below 180-200. For these conditions, $P$ increased (i.e. axial dispersion decreases) with the presence of fluid oscillations, from a value of about 6 in the absence of oscillations to a value of about 20 (i.e. about 30 % of decrease of axial dispersion) achieved at a $Re_o$ of ca. 180 ($f$ = 7.5 Hz and $x_0$ = 1 mm). This is believed to be related with the break of flow symmetry as reported by previous studies (Harvey et al., [2]) in the SPC tube. Ni and Pereira [12] reported a 25 % lower dispersion for a fluid oscillated inside a conventional OFR when compared with the flow in a plain pipe.

The best oscillation conditions for a near plug flow behaviour were found to be oscillation amplitudes from 0.5 to 1 mm and frequencies from 7.5 to 10 Hz. The near completely mixed state can be accomplished at high oscillation amplitudes (> 3 mm) and frequencies (> 20 Hz), due to high backflow rates.

## CONCLUSIONS

Fibre optics have been successfully applied in the determination of residence time distributions in a small-scale tube provided with smooth periodic constrictions which is the base unit of a novel oscillatory flow screening reactor envisaged for two and three-phase flows. An intermediate mixing behaviour was obtained at oscillation conditions up to 20 Hz and 3 mm centre-to-peak. This was related to the vortex rings and eddy structures formed in the reactor, which produce convective mixing in the direction of the flow [20], according to previously reported studies on the screening reactor [2].

It has been demonstrated that a RTD analysis in the Laplace domain generates reproducible results and allows fitting theoretical models that would otherwise be very difficult to test in the time domain. Considering the presence of discrete cavities and the observed good local mixing within each cavity as previously reported by Harvey *et al*. [2], the discrete stagewise mixing model appears to give a better physical description of flow within the small-scale tube than that of a continuous plug flow with axial dispersion.

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## NOMENCLATURE

$d$ mean internal tube diameter, m
$D$ dispersion coefficient, $m^2/s$
$f$ oscillation frequency, Hz
$G$ backmixing ratio, dimensionless
$l$ axial distance, m
$L$ reactor lenght, m
$N$ total number os discrete tanks, dimensionless
$n$ stage number, dimensionless
$P$ Peclet number (= $u\,L/D$; $u$ is fluid velocity in m/s), dimensionless
$Re_o$ oscillatory Reynolds number ($=2pfx_0 rd/m$, with $x_0$ in mm), dimensionless
$t$ time, s
$\bar{t}$ mean residence time of the tracer, s
$T$ Laplace's variable, dimensionless
$v$ volumetric flow rate, $m^3/s$
$V$ reactor volume, $m^3$
$x$ tracer concentration, kg/$m^3$
$\bar{x}$ Laplace's transform of the pulse response, dimensionless
$x_0$ oscillation amplitude, mm

*Subscripts*

in incoming ($x$)
m completely mixed region
out outgoing ($x$)
p plug region
sw stagewise model
tis tanks-in-series model

*Greek symbols*

$m$ fluid viscosity, kg/(m s)
$q$ dimensionless time = $t/\bar{t}$
$r$ density of the fluid, kg/$m^3$
$s^2$ variance, $s^2$

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